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APPLICATION FOR LETTERS PATENT

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LOW SELECTIVITY DEPOSITION METHODS

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LOW SELECTIVITY DEPOSITION METHODS

TECHNICAL FIELD

This invention relates to methods of atomic layer deposition and methods of low selectivity chemical vapor deposition.

BACKGROUND OF THE INVENTION

Atomic layer deposition (ALD) is recognized as a deposition technique that forms high quality materials with minimal defects and tight statistical process control. Even so, it is equally recognized that ALD can have limited application. In some circumstances, the theoretically expected quality of an ALD layer is not achieved.

It can be seen that a need exists for an ALD method that forms a layer without introducing intolerable defects into the material.

BRIEF DESCRIPTION OF THE DRAWINGS

Preferred embodiments of the invention are described below with reference to the following accompanying drawings.

Fig. 1 shows a cross-sectional fragmentary view of a deposition substrate at one processing step in accordance with an aspect of the invention.

Fig. 2 shows the deposition substrate of Fig. 1 at a processing step subsequent to that shown in Fig. 1.

1 Fig. 3 shows the deposition substrate of Fig. 1 at an alternative
2 processing step subsequent to that shown in Fig. 1.

3 Fig. 4 shows the deposition substrate of Fig. 1 at a processing step
4 subsequent to that shown in Fig. 3.

5 Fig. 5 shows a cross-sectional fragmentary view of a semiconductive
6 wafer portion at a processing step in accordance with an aspect of the
7 invention.

8 Fig. 6 shows the semiconductive wafer of Fig. 5 at a processing
9 step subsequent to that shown in Fig. 5.

10 11 SUMMARY OF THE INVENTION

12 One aspect of the invention provides a deposition method that
13 includes forming a nucleation layer over a substrate, forming a layer of
14 a first substance at least one monolayer thick chemisorbed on the
15 nucleation layer, and forming a layer of a second substance at least one
16 monolayer thick chemisorbed on the first substance. A chemisorption
17 product of the first and second substance may include silicon and
18 nitrogen, or aluminum and oxygen, or tantalum and oxygen. Also, the
19 nucleation layer may comprise silicon nitride, aluminum oxide, or
20 tantalum oxide. A thickness of the nucleation layer may be less than
21 about 20 Angstroms.

22 In another aspect of the invention, a low selectivity deposition
23 method includes forming a first part of a nucleation layer on a first

surface of a substrate and forming a second part of a nucleation layer on a second surface of a substrate. A deposition layer may then be formed on the first and second parts of the nucleation layer substantially non-selectively on the first part of the nucleation layer compared to the second part. Substantially non-selective deposition occurs even though the first and second surfaces of the substrate exhibit a property of the deposition layer forming less readily on the first surface compared to the second surface. The deposition layer may comprise a monolayer of a first chemisorbed specie. The deposition layer may be formed by chemical vapor deposition or atomic layer deposition. The first and second part of the nucleation layer may be formed simultaneously. Also, the nucleation layer may form substantially non-selectively on the first surface of the substrate compared to the second surface. Further, a thickness of the first part of the nucleation layer may be greater than 50% of a thickness of the second part, or even greater than 80% of the thickness of the second part. The first surface of the substrate may exhibit a property of chemisorbing the first specie at a slower rate compared to the second surface.

In another aspect, a deposition method includes simultaneously forming a first part of a nucleation layer on an insulative oxide material and a second part of the nucleation layer on a semiconductive material. The nucleation layer may be contacted with an initiation precursor. An initiation layer at last one monolayer thick may be formed on the first

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1 and second parts of the nucleation layer substantially non-selectively on
2 the first part of the nucleation layer compared to the second part.

3 In another deposition method, a nucleation layer comprising silicon
4 and nitrogen may be formed substantially non-selectively on a first and
5 a second surface of a substrate. A monolayer of a first substance may
6 be chemisorbed on the nucleation layer. A monolayer of a second
7 substance may be chemisorbed on the first substance, wherein a
8 chemisorption product of the first and second substances comprises
9 silicon nitride.

10 In a still further aspect, a deposition method may include atomic
11 layer depositing a nucleation substance chemisorbed on a first surface
12 and a second surface of a substrate substantially non-selectively. The
13 first surface may exhibit a property of chemisorbing an atomic layer
14 deposition precursor at a slower rate compared to the second surface.
15 Also, the nucleation substance may exhibit a property of chemisorbing
16 the precursor at an approximately equal rate over the first surface
17 compared to over the second surface.

18 19 DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

20 This disclosure of the invention is submitted in furtherance of the
21 constitutional purposes of the U.S. Patent Laws "to promote the progress
22 of science and useful arts" (Article 1, Section 8).
23

Atomic layer deposition (ALD) involves formation of successive atomic layers on a substrate. Such layers may comprise an epitaxial, polycrystalline, amorphous, etc. material. ALD may also be referred to as atomic layer epitaxy, atomic layer processing, etc. Further, the invention may encompass other deposition methods not traditionally referred to as ALD, for example, chemical vapor deposition (CVD), but nevertheless including the method steps described herein. The deposition methods herein may be described in the context of formation on a semiconductor wafer. However, the invention encompasses deposition on a variety of substrates besides semiconductor substrates.

In the context of this document, the term "semiconductor substrate" or "semiconductive substrate" is defined to mean any construction comprising semiconductive material, including, but not limited to, bulk semiconductive materials such as a semiconductive wafer (either alone or in assemblies comprising other materials thereon), and semiconductive material layers (either alone or in assemblies comprising other materials). The term "substrate" refers to any supporting structure, including, but not limited to, the semiconductive substrates described above.

Described in summary, ALD includes exposing an initial substrate to a first chemical specie to accomplish chemisorption of the specie onto the substrate. Theoretically, the chemisorption forms a monolayer that is uniformly one atom or molecule thick on the entire exposed initial

create thickness variations in the deposited material. Also, for example, a desire may exist to simultaneously deposit a material over two dissimilar types of substrate. A surface of borophosphosilicate glass (BPSG) and a surface of polysilicon can be two dissimilar types of substrate. Observations indicate that formation of silicon nitride by ALD simultaneously on BPSG and polysilicon produces a thickness variation in the deposited silicon nitride. The thickness of the silicon nitride deposited on the BPSG can be less than 50% of the thickness of the silicon nitride deposited on the polysilicon. A variety of other circumstances are conceivable wherein a substantially uniform thickness of a material deposited by ALD is desired on dissimilar portions of a substrate, such as a semiconductive substrate compared to an insulative or a conductive substrate.

According to one aspect of the invention, a deposition method may include forming a nucleation layer over a substrate. The nucleation layer may exhibit a first value of an electrical property, for example, dielectric constant, conductivity, current leakage, permittivity, capacitance, etc. Turning to Fig. 1, a substrate 2 is shown including a first part 4 and a second part 6. Second part 6 may comprise a composition different from first part 4 or second part 6 may comprise the same composition but exhibit a property that causes deposition to occur more readily on second part 6 compared to first part 4. Fig. 2 shows a deposition layer 8 formed on first part 4 and second part 6 of substrate 2. Notably, the

1 thickness of deposition layer 8 that is over first part 4 is less than 50%
2 of a thickness of deposition layer 8 that is over second part 6.

3 There can be at least one advantage of providing a nucleation
4 layer over a substrate prior to performing some types of deposition, for
5 example ALD. The nucleation layer may operate to provide at least
6 somewhat uniform surface properties for the deposition and decrease
7 thickness variations such as shown in Fig. 2. Even so, a nucleation layer
8 may interface between a substrate and a subsequently deposited
9 deposition layer in a manner that only insignificantly influences the
10 overall properties of the combined nucleation and deposition layer. That
11 is, a deposition layer deposited directly on a substrate without a
12 nucleation layer generally will possess some designated purpose or
13 designated property. A nucleation layer may be selected such that only
14 an insignificant impact is imposed upon the desired purpose or property.
15 Accordingly, a nucleation layer may find advantageous use even in
16 circumstances where a substrate possesses both a homogeneous
17 composition and homogeneous surface properties. Such a nucleation
18 layer may interface between a substrate and a deposition layer to
19 enhance the rate of formation of the deposition layer or to otherwise
20 provide an advantageous property or result. For example, a first
21 monolayer of a first chemisorbed specie may form more rapidly over
22 BPSG if a nucleation layer is first formed.

In addition to composition and surface properties, the thickness of a nucleation layer may also influence its suitability. At times, ALD is selected with the desire to form high quality very thin layers of material. A nucleation layer may be selected that only insignificantly impacts the deposition layer. However, as the thickness of a nucleation layer increases and approaches or exceeds the thickness of a deposition layer, the potential advantages of selecting ALD for forming a layer of the material may be diminished. At the optimum, a nucleation layer having a thickness of only one atom or molecule may be formed to minimize any potential impact. However, a more thick nucleation layer may also provide little impact. Accordingly, a thickness of a nucleation layer may comprise less than about 20 Angstroms. Further, the thickness may comprise less than about 6 Angstroms. Still further, the thickness may comprise about 2.5 Angstroms. A monolayer of silicon nitride may comprise about 2.5 Angstroms.

In Fig. 3, a nucleation layer 10 is shown formed over substrate 2. In the illustration provided, substrate 2 includes first part 4 on which deposition occurs less readily compared to second part 6. As indicated, such a property may be caused by first part 4 possessing a different composition than second part 6 or exhibiting a different surface property than second part 6. Such is in contrast to another advantageous use of nucleation layer 10 even when a substrate possesses homogeneous composition and exhibits homogeneous surface properties.

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As shown in Fig. 4, a deposition layer 12 may be formed on nucleation layer 10 without the thickness variation illustrated in Fig. 2. Deposition layer 12 may be formed by any deposition method presently known to those skilled in the art or later developed, but preferably by ALD as defined herein. Other deposition methods may also be suitable. In the present aspect of the invention, a suitable deposition method may include forming a layer of a first substance at least one monolayer thick chemisorbed on the nucleation layer and forming a layer of a second substance at least one monolayer thick chemisorbed on the first substance. A chemisorption product of the layers may comprise deposition layer 12. Deposition layer 12 may exhibit a second value of the electrical property exhibited by nucleation layer 10 at a first value. Examples of electrical properties are listed above. Deposition layer 12 and nucleation layer 10 combined may exhibit a third value of the electrical property that is more near the second value than the first value. The third value and second value may be approximately equal. The method may include at least once additionally forming successive monolayers of the first substance and the second substance. In such case, all monolayers may be comprised by deposition layer 12.

Nucleation layer 10 may possess a variety of compositions and exhibit a variety of properties and still comprise a suitable interface between deposition layer 12 and a substrate, for example substrate 2. For example, nucleation layer 10 may comprise a compound the same as

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1 a deposition product of the first and second substances in the
2 chemisorbed monolayers described above. For example, a chemisorption
3 product of the first and second substance may comprise silicon and
4 nitrogen. A nucleation layer may also comprise silicon and nitrogen.
5 More specifically, the chemisorption product that produces deposition
6 layer 12 may comprise silicon nitride and nucleation 10 may also
7 comprise silicon nitride.

8 A nucleation layer may comprise an approximately homogeneous
9 composition. In an approximately homogeneous composition, only
10 insignificant differences in composition exist throughout the nucleation
11 layer. However, a nucleation layer may also possess a composition
12 wherein one part of the nucleation layer differs from a composition of
13 another part of the nucleation layer as to a component, a proportion of
14 a component, or both. One example is a nucleation layer that comprises
15 silicon nitride but a part of the nucleation layer further comprises
16 oxygen, for example, comprising silicon oxynitride.

17 In another aspect of the invention, a deposition method includes
18 forming a first part of a nucleation layer on a first surface of a
19 substrate and forming a second part of a nucleation layer on a second
20 surface of the substrate. Forming the first and second part of the
21 nucleation layer may occur simultaneously. Alternatively, the first part
22 and the second part of the nucleation layer may be formed separately.
23 When formed simultaneously, the nucleation layer may form substantially

1 non-selectively on the first surface of the substrate compared to the
2 second surface. The thickness of a nucleation layer is one measure of
3 the selectivity of forming a nucleation layer. That is, non-selective
4 formation of a nucleation layer may occur when the thickness of the first
5 part of the nucleation layer on the first surface of a substrate is greater
6 than 50% of the thickness of the second part formed on the second
7 surface of the substrate. More particularly, non-selective formation
8 occurs when the thickness of the first part is greater than 80% of the
9 thickness of the second part.

10 One advantage of the present invention is that substantially non-
11 selective formation of a nucleation layer may occur even though ALD on
12 the same surface occurs selectively, that is, at a greater than 2 to 1
13 ratio of deposition rate. Such a deposition may produce a deposition
14 layer having a thickness over the first surface that is less than 50% of
15 the thickness over the second surface.

16 A variety of nucleation layer compositions are conceivable just as
17 a variety of nucleation layer thicknesses and selectivities are conceivable.
18 The second part of the nucleation layer on the second surface of the
19 substrate may comprise a plurality of components also comprised by the
20 first part. For example, the first and second parts of the nucleation
21 layer may comprise silicon nitride. Further, the first and second parts
22 of the nucleation layer may even consist essentially of the same
23 components in approximately same proportions. For example, the first

and second parts of the nucleation layer may comprise an approximately homogeneous composition. However, the composition of the first part of the nucleation layer may also differ from the composition of the second part of the nucleation layer. In such a circumstance, the first and second parts of the nucleation layer may still both comprise silicon nitride. In addition, the first part may further comprise oxygen, for example, as in silicon oxynitride.

The present aspect of the invention may further include forming a monolayer of a first chemisorbed specie on the first and second parts of the nucleation layer substantially non-selectively on the first part of the nucleation layer compared to the second part. Such non-selective formation of a monolayer of a first chemisorbed specie may occur even though the first surface of the substrate exhibits a property of chemisorbing the first specie at a slower rate compared to the second surface. This circumstance indicates one advantage of the present aspect of the invention. Namely, the nucleation layer may operate to interface between a deposition layer and a substrate to alter properties such that deposition occurs substantially non-selectively. The deposition method may further comprise forming a monolayer of a second chemisorbed specie different from the first specie on the first specie layer. It may be advantageous that the nucleation layer comprise a material also comprised by the first and second specie layers combined. For example, the first and second specie layers, in combination, may comprise silicon

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1 monolayer of a first chemisorbed precursor may then be formed on the
2 nucleation layer also by ALD.

3 Often, traditional ALD occurs within an often-used range of
4 temperature and pressure and according to established purging criteria
5 to achieve the desired formation of an overall ALD layer one monolayer
6 at a time. Even so, ALD conditions can vary greatly depending on the
7 particular precursors, layer composition, deposition equipment, and other
8 factors according to criteria known by those skilled in the art.
9 Maintaining the traditional conditions of temperature, pressure, and
10 purging minimizes unwanted reactions that may impact monolayer
11 formation and quality of the resulting overall ALD layer. Accordingly,
12 operating outside the traditional temperature and pressure ranges may
13 risk formation of defective monolayers.

14 In accordance with the present aspect of the invention, observations
15 indicate that increasing temperature or pressure or both can produce the
16 effect of reducing the selectivity of an otherwise selective monolayer
17 formation step. In the various aspects of the invention, temperature may
18 remain below about 550 Celsius ($^{\circ}\text{C}$) and pressure may remain below
19 about 20 Torr. The increased temperature, pressure, or both
20 correspondingly increases the likelihood that a deposition specie will
21 chemisorb substantially non-selectively on the first and second surfaces
22 of the substrate as described above and shown in Fig. 3. Even though
23 such a process regime risks defective monolayer formation, such process

may be used to form a nucleation layer by ALD. The deposition layer may be formed in a traditional ALD process regime at lower temperature and pressure. For example, traditional ALD of silicon nitride may occur at a temperature of from about 400 °C to about 550 °C and a pressure of less than about 100 milliTorr. Different ranges are also conceivable, as determinable by those skilled in the art, depending on deposition precursors, nucleation layer composition, surface properties, and other factors. Depending on the desired properties of the deposition layer, such layer may also be formed by ALD outside the traditional ALD process regime.

Another example of an *in situ* method involves chemical vapor deposition (CVD). The general technology of CVD includes a variety of more specific processes, including, but not limited to, plasma enhanced CVD and others. CVD is commonly used to form non-selectively a complete, deposited material on a substrate. One characteristic of CVD is the simultaneous presence of multiple species in the deposition chamber that react to form the deposited material. Such condition is contrasted with the purging criteria for traditional ALD wherein a substrate is contacted with a single deposition specie and chemisorbs to a substrate or previously deposited specie. A nontraditional ALD process regime may provide simultaneously contacted species of a type or under conditions such that ALD chemisorption, rather than CVD reaction occurs.

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1 As one example, U.S. Patent Application No. 09/619,449 filed July
2 19, 2000 by Garo J. Derderian and Gurtej S. Sandhu entitled
3 "Deposition Methods" and assigned to Micron Technologies, Inc. discloses
4 a nontraditional ALD process and is herein incorporated by reference.
5 Derderian et al. describe a deposition method including contacting a
6 substrate with a first initiation precursor and forming a first portion of
7 an initiation layer on the substrate. At least a part of the substrate is
8 contacted with a second initiation precursor different from the first
9 initiation precursor and a second portion of the initiation layer is formed
10 on the substrate. The invention may include simultaneously contacting
11 a substrate with a plurality of initiation precursors, forming on the
12 substrate an initiation layer comprising components derived from each of
13 the plurality of initiation precursors. However, the plurality of initiation
14 precursors do not react together as in CVD. Rather, they chemisorb to
15 the substrate, providing a surface onto which a deposition specie may
16 next chemisorb to form a complete layer of desired material.

17 Under most CVD conditions, deposition of the material occurs
18 largely independent of the composition or surface properties of an
19 underlying substrate. However, deposition rate can be a frequent issue
20 in performing CVD. High deposition rates are often desired to increase
21 production output as long as such rates do not significantly diminish the
22 quality of a deposited material. Accordingly, depending on the particular
23 type of CVD technique, a process regime is selected that produces as

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1 high a deposition rate as is possible without significant negative impacts
2 on material quality.

3 In the present aspect of the invention, deposition rate is a less
4 significant issue. Accordingly, observation indicates that lower pressures,
5 temperatures, plasma intensities, reactant concentrations, etc., than would
6 otherwise be traditionally accepted may be used to produce a nucleation
7 layer. CVD of a nucleation layer may thus occur at a deposition rate
8 that conventionally might not qualify for a suitable CVD process. For
9 example, traditional CVD of silicon nitride may occur at a temperature
10 between about 600 °C to about 800 °C and a pressure between about
11 100 milliTorr to about 2 Torr, depending on the selected temperature.
12 If temperature is toward the low end of the range, then pressure is
13 generally toward the high end of the range to stay within the traditional
14 process regime. Exemplary parameters for nontraditional CVD of a
15 nucleation layer may fall below one or both of such ranges or be in the
16 low end of both ranges. Different ranges are conceivable, as
17 determinable by those skilled in the art, depending on deposition
18 precursors, substrate composition, surface properties, and other factors.

19 Since CVD is typically a non-selective form of deposition, the non-
20 traditional process regime can produce a suitable nucleation layer having
21 a thickness of one atom or molecule or more. Specifically, formation
22 of an approximately 4 to 6 Angstrom silicon nitride nucleation layer from
23 ammonia and dichlorosilane (DCS) has been achieved at a pressure of

As examples of *ex situ* processing, any of the above-described ALD or CVD techniques may be used. A substrate may be placed in a first chamber and the first and second parts of a nucleation layer formed on the substrate. The substrate may then be removed from the first chamber and placed in a second chamber different from the first. Formation of an ALD precursor monolayer or unconventional CVD layer may then occur in the second chamber. Accordingly, the first chamber may comprise any tool suitable for accomplishing CVD or ALD.

The first chamber may further comprise any tool suitable for accomplishing techniques such as rapid thermal nitridation (RTN), remote plasma nitridation (RPN), techniques for accomplishing growth of a material (as opposed to deposition) on a substrate, and other techniques. RTN, RPN, and other techniques can involve growth of a nucleation layer non-selectively on first and second surfaces of a substrate. RTN often occurs in an ammonia ambient at a temperature of greater than 700°C. Temperature may be limited to about 800°C in circumstances where thermal budget limitations exist. RPN is performed similarly except that a plasma is used to provide reactive nitrogen radicals in a manner that provides reduction of process temperature. Accordingly, RPN may be preferred in a circumstance with a sensitive thermal budget.

Material growth techniques, for example RTN, RPN, and others, may produce a nucleation layer the composition and selectivity of which can be influenced by the composition of the underlying substrate. For

may subsequently occur on the *ex situ* formed nucleation layer also substantially non-selectively.

Another aspect of the invention holds specific application to forming container capacitor structures. Fig. 5 shows a semiconductive wafer construction 20 having partially formed dynamic random access memory (DRAM) cells formed thereon. Semiconductive wafer construction 20 includes a semiconductive material 22, for example, a bulk silicon wafer, and a field oxide 23 formed on semiconductive material 22. Node locations 25, 27, and 29 are formed within semiconductive material 22. Word lines 24 are formed over field oxide 23 and word lines 26 are formed over semiconductive material 22. An oxide layer 32 formed over word lines 24 and 26 prevents diffusion of dopants within a BPSG layer 34 into word lines 24 and 26. Capacitor openings 38 and 40 are formed through BPSG layer 34 to expose node locations 25 and 29, respectively. A storage node layer 36 is formed on BPSG layer 34 and in electrical connection with node locations 25 and 29. Storage node layer 36 may comprise polysilicon, or more preferably rugged polysilicon. Rugged polysilicon may include hemispherical grain polysilicon, spherical grain polysilicon, etc.

Formation of silicon nitride as a capacitor dielectric on storage node layer 36 is desired. Formation of silicon nitride on BPSG layer 34 as a dopant diffusion barrier is also desired. Formation of silicon nitride as a capacitor dielectric by ALD offers the advantage of a thin

capacitor layer that possesses low electrical tunneling probability and low defect densities compared to traditional CVD silicon nitride. Simultaneous formation of silicon nitride over storage node layer 36 and BPSG layer 34 would also afford processing advantages. As described above, observation indicates that ALD of silicon nitride forms preferentially on polysilicon compared to BPSG. Accordingly, the various aspects of the present invention allow formation of a nucleation layer (not shown due to its preferably small thickness) on storage node layer 36 and BPSG layer 34 followed by formation of a deposition layer 42 as shown in Fig. 6 on the nucleation layer. The nucleation layer may be formed simultaneously and non-selectively on storage node layer 36 and BPSG layer 34. The nucleation layer may comprise silicon nitride, but may instead comprise some other compound. Accordingly, the nucleation layer may comprise a material that is not a suitable capacitor dielectric and/or dopant diffusion barrier.

Examples of process conditions for forming nucleation layers depends on the type of formation process and desired properties of the layer in keeping with the aspect of the invention described above. A silicon nitride nucleation layer may be formed *in situ* in a low pressure CVD hot wall batch reactor at about 645 °C and about 1.5 Torr. Processing time may be varied to form a layer of a thickness suitable for nucleation. Subsequently, a deposition layer may be formed on the

1 nucleation layer within the low pressure CVD hot wall batch reactor.
2 The deposition layer may be formed by ALD.

3 Alternatively, a silicon nitride nucleation layer may be formed *ex*
4 *situ* using RTN at about 800 °C for about 60 seconds in an ammonia
5 ambient. The substrate and nucleation layer may then be removed to
6 a deposition device suitable for the deposition layer formation, such as
7 by ALD.

8 In compliance with the statute, the invention has been described
9 in language more or less specific as to structural and methodical
10 features. It is to be understood, however, that the invention is not
11 limited to the specific features shown and described, since the means
12 herein disclosed comprise preferred forms of putting the invention into
13 effect. The invention is, therefore, claimed in any of its forms or
14 modifications within the proper scope of the appended claims
15 appropriately interpreted in accordance with the doctrine of equivalents.
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